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COMPLETE SPECIFICATION

Improvements in or relating to Insecticidal Compositions, and Packaging Materials Coated therewith

We, COOPER, MCDOUGALL & ROBERTSON LIMITED, a Company incorporated in England, of Chemical Works, Berkhamsted, Hertfordshire, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention concerns improvements in or relating to insecticidal compositions, and packaging materials coated therewith.

In the field of packaging materials it has long been recognised that there is a need to provide surface coatings on paper, cardboard and like fibrous packaging material which will furnish protection for the contents of the package against infestation by insect pests, particularly of course during storage. The problem posed by insect infestation is most acute in the case of packaging for human foodstuffs, but similar problems can arise with other items intended for human consumption such as tobacco, and also with animal foodstuffs. The call for insecticide-impregnated packaging has been met for some years by the use of an amine alginate/pybuthrin coating composition which is the subject of our Patent No. 895,455 — but that coating composition, though eminently satisfactory in other respects, gives the packaging material a dull, matt appearance, commonly called a "flat-finish."

There is today an increasing demand by manufacturers of food products for glossy cartons and other packaging materials, and the insecticidal coating compositions that we have been able till now to prepare have at best yielded only a semi-matt or satin finish, while to date any additive which might have been expected to give an improved finish has tended to reduce the insecticidal activity of the coating. The call for glossy coating compositions displaying insecticidal activity has not been met adequately by previous suggestions for incorporating insecticides in a synthetic resin base; the compositions which have been tried when effective to release the insecticide for performance of its function, tend to exhibit a matt appearance. Presumably this is because the insecticide release mechanism involves crazing of the thin film of synthetic resin coated onto the packaging material, and efflorescence of the insecticide from these cracks onto the surface. Whether or not this presumption is correct, the facts show that previously proposed synthetic resin-based insecticidal coating compositions impart a "flat-finish" just as do the amine alginate/pybuthrin compositions in widespread use.

We have now found, however, that by careful selection of the synthetic resins employed as the resin base for the coating, it is possible to produce insecticidal synthetic resin coating compositions for use on fibrous packaging material which meet modern requirements, and which in particular are effective to release the insecticide, yet at the same time impart and sustain a durable glossy finish on the paper, board or other packaging material.

According to the present invention in one aspect, there are provided insecticidal coating compositions, especially adapted for use upon fibrous packaging material such as paper, cardboard and the like, comprising one or more insecticides dissolved and/or dispersed in a film-forming synthetic resin consisting wholly or predominantly of a copolymer of styrene with a dibasic unsaturated aliphatic acid half-ester.

The compositions of this invention are, as in explained in more detail hereinafter, of particular use in the protection of packaging materials employed for the containment of food

stuffs. It is therefore of especial importance that these particular compositions are non-toxic or humans — and to domestic livestock in general — and therefore the especially preferred insecticides are those having an LD_{50} (rat: oral) of at least 400 mg/kg and desirably 500 mg/kg, or preferably greater. Of these, the outstanding insecticides of low mammalian toxicity are the pyrethrinoids, which are reported (*vide* A. J. Lehman, *Quarterly Bull. of Assoc. of Food & Drug Officials of the U.S.A.*, (1948), *12*. p.82) to have an average oral LD_{50} (for all of the various animals tested) of 1500 mg/kg bodyweight.

In particular therefore, according to the present invention, there are provided insecticidal coating compositions, especially adapted for use upon fibrous packaging material such as paper, cardboard and the like, comprising one or more of the pyrethrinoid insecticides dissolved and/or dispersed in a film-forming synthetic resin consisting wholly or predominantly of a copolymer of styrene with a dibasic unsaturated aliphatic acid half-ester.

By the term "pyrethrinoid insecticide" we mean esters of 2,2 - dimethyl - 3 - substituted-cyclopropane - carboxylic acids; the term is not necessarily limited to compounds found in vegetable extracts but naturally extends to similar or equivalent synthetic compounds. By way of example, the 3-substituent may be that occurring in the insecticide known as Pyrethrin 1, or Pyrethrin 2. Allethrin is a specific example of a suitable pyrethrinoid insecticide.

The insecticidal compositions of this invention are alcohol-soluble, a fact which is of great importance in paper technology since it facilitates their application to the web of paper, cardboard or the like, by conventional paper-coating machinery. The compositions furthermore are almost water-white in colour, so that they do not adversely affect the appearance of the paper, cardboard or like web; this remains true whether the compositions are applied before or after printing though it is to be noted that printing will normally be carried out before coating, which in fact will usually be the last operation carried out on the packaging material. Prolonged tests on the resin base have moreover shown that, so far as can be judged by visual examination, the compositions after application to the paper, cardboard or like web are completely non-yellowing within the foreseeable shelf-life of the product.

Still further, the surface coatings produced on paper, cardboard or like reasonably non-porous webs are glossy in appearance despite the quick drying characteristics of these compositions when applied by conventional paper coating techniques in the form of solutions in highly volatile alcoholic solvents. This glossy appearance, which is highly valued in modern packaging, is moreover maintained apparently indefinitely, and is not impaired by any visible crazing or cracking, yet the insecticide incorporated in the composition before application seems nevertheless to be released in sufficient quantity over a prolonged period adequately to safeguard the contents of packages made from this impregnated paper, cardboard or the like against attack by insect pests. It is moreover a major advantage of the compositions of the invention that packaging material coated with them displays good water and grease-resistance, usually considerably superior to that of the "flat-finish" insecticidal coating compositions used hitherto for the same purpose. Although not always of importance, it is also noteworthy that the compositions of the invention form surface coatings which withstand deep-freeze storage conditions outstandingly well.

As indicated above, the compositions of this invention may contain any insecticide suitable for the purpose to which the composition-coated packing material ultimately may be put. The insecticides incorporated in these compositions can therefore be either liquid or solid, but when employing solid insecticides a co-solvent may be required to ensure complete solubility of the insecticide in the synthetic resin base. The range of insecticides which may be incorporated thus includes pyrethrum, neopynamin, malathion, allethrin, vapona, sevin, bromophos and sumithion. The amount of each insecticide incorporated will be a function of the biological activity of the compound and the nature of the insect pest most likely to be encountered.

The primary use currently envisaged for the compositions of the invention is in the coating of paper or cardboard packaging materials for foodstuffs, and, therefore, the insecticides of choice for use with the compositions of this invention are those most suited for use in such a milieu; above all pyrethrum and other pyrethrinoid insecticides as herein defined (thus including neopynamin and allethrin), or mixtures thereof with the synergists based on the methylene dioxy phenyl structure, notably the synergist known as piperonyl butoxide. Although emphasis is laid here on the use of the synergists just mentioned, we do not mean to exclude the use of other synergists, such as sulfoxide and safroxan (more systematically named 4 - (3,4 - methylene - dioxyphenyl)-5 - methyl - meta - dioxane).

The common chlorinated insecticides are today regarded as a health hazard, whereas no dangers to health have been observed consequent on the use of the naturally-occurring insecticidal vegetable-extract pyrethrum, either in its own right or in the preferred form in which it is utilised in the compositions of this invention, namely the synergistic mixture of pyrethrum with piperonyl butoxide, commonly known and herein referred to as "pybuthrin".

A point of interest and important is that, although pybuthrin is itself a liquid at normal

temperature, and moreover is relatively unstable and short-acting as an insecticide, when incorporated in the compositions of the present invention it nevertheless yields coatings on paper, cardboard and the like which display excellent insecticidal activity over a prolonged period.

The insecticide and the resin base may be admixed to form the compositions of this invention in any convenient proportions. We have not found it necessary for the insecticide to be present in an amount exceeding the solvent power of the synthetic resin base — though such a supersaturation is not excluded from the invention should it be desired. The optimum proportions to achieve any particular biological result with specified insecticides and resin based can of course be determined by standard experimental techniques. The components of the composition may be admixed as desired, but where necessary or convenient will be incorporated in the form of a solution in a suitable organic solvent similar to or compatible with the other solvents employed. One such solvent which we have found generally useful is *iso*propyl alcohol.

For ease of application to the packaging material, the compositions should be so formulated as to have a similar viscosity to that of conventional spirit varnishes used as overprint coatings, and be thus suitable for use, without further dilution, on paper varnishing machines, such as the Bush or Gula. Accordingly the compositions will normally be thinned to a suitably viscosity by inclusion of a predominant proportion of one or more highly volatile alcoholic solvents. Generally, however, we have found that a viscosity sufficient to allow a full discharge time of between 25 and 100 seconds from a No. 4 Ford Cup (British Specification No. 1733, Type B4) is suitable for the various different types of applicator likely to be met. This is approximately equivalent to a viscosity range of 40 to 220 centipoises.

A typical formulation of this product would be 55 parts by weight of an alcoholic solution of resin base per 45 parts by weight of an alcoholic solution of the insecticide. In general, the use of an alcoholic solution containing 55% by weight of resin base will yield a final composition of the desired viscosity, but for certain purposes it may be necessary to thin this formulation still further by the addition of even more alcohol.

Provided that the resin base employed is a co-polymer of styrene with a dibasic unsaturated aliphatic acid half-ester, the proportions of the two co-polymerizing components in the resin base are not highly critical. For guidance it may however be said that the two co-polymerizing components will normally be present in an overall range of proportions of from 20/80 to 80/20 weight parts, while to secure the best film-forming properties the proportions are desirably kept within the range of 60/40 to 40/60 parts by weight. Usually it is most convenient to aim at equimolar proportions, which roughly are represented by a 50/50 ratio by weight.

The dibasic unsaturated aliphatic acid employed to form the half-ester may be chosen at will from vinylic dicarboxylic acids, including for instance fumaric acid, but we prefer to employ maleic acid desirably, in the form of its anhydride. The dibasic unsaturated aliphatic acid must be employed in the form of its half-ester, since it lacks adequate alcohol solubility when either unesterified or fully esterified. While half-esters formed with any of the great variety of commercially available alcohols are believed to be suitable, we have found that in practice all the variations in properties which may be desired in a "tailor-made" product may be attained by suitable selection of primary aliphatic alcohols, usually but not necessarily unsubstituted straight-chain alcohols, having from 1 to 18 carbon atoms. Moreover, within that broad range we have found that for most practical purposes it is only necessary to employ alcohols with from 1 to 9 carbon atoms, while preferably the alcohols employed have from 1 to 5 carbon atoms, the specific preferred alcohols being those with 2 to 4 carbon atoms, and especially ethanol and *n*-butanol.

The styrene component will be employed usually in the form of styrene monomer alone, but the use of styrene monomer admixed with a minor proportion of any other compatible vinylic monomer or mixed monomers, such as methylmethacrylate, ethylmethacrylate, butyacrylate, ethylhexylacrylate and so on, is not excluded.

The resin component of the compositions of this invention will desirably incorporate a cross-linking catalyst, advantageously in the form of a peroxide. A variety of peroxides have been shown to be satisfactory, including for instance methylethyl peroxide, but the preferred catalyst is benzoyl peroxide.

In order that the invention may be well understood the following examples will now be given, though only by way of illustration, to show certain preferred insecticidal glossy coating compositions. It should be noted that in these examples commercially-available ingredients have been employed where possible, and for convenience have been referred to by their common or proprietory names, as indicated below:—

The film-forming synthetic resins identified as KELREZ SS.11 and SS.34 are available commercially and are both understood to be a 55% solution in *iso*propanol/ethanol of a styrene/butyl acid maleate copolymer, differing mainly in their viscosities. References to these commercial products are to be understood as designating them as sold, thus as indicating the use of an alcoholic solution of

the resin rather than the use of that amount of the resin itself.

Pyrethrum is the common name for the vegetable extract containing insecticidal pyrethrins. Mixtures of pyrethrum with the synergist a — (2 - (2 - butoxyethoxy)ethoxy) - 4,5 - methylenedioxy - 2 - propyl - toluene, commonly known as piperonyl butoxide, are sold under the Registered Trade Mark "PYBUTHRIN."

The insecticide 3,4,5,6 - tetrahydrophthalimidomethyl - ester of chrysanthumic acid is available under the Registered Trade Mark "NEOPYNAMIN". The insecticide O,O-dimethyl - S - (1,2 - dicarbethoxyethyl) - phosphorodithioate is available under the Registered Trade Mark "MALATHION". Allethrin is the approved open name of a synthetic insecticide closely related in chemical structure to the pyrethrins. The insecticide a - naphthyn - N - methylcarbamate is available under the Registered Trade Mark "SEVIN". The insecticide *O,O* - dimethyl-O - (4 - bromo - 2,5 - dichlorophenyl) - phosphorothionate is available under the trade name "BROMOPHOS". The insecticide *O,O*-dimethyl - *O* - (3 - methyl - 4 - nitrophenyl)-phosphoro - thionate is available under the Registered Trade Mark "SUMITHION".

EXAMPLES: INSECTICIDAL GLOSSY COATING COMPOSITIONS

EXAMPLE I

Styrene/butyl acid maleate copolymer	30.25 parts by weight
Pyrethrum extract (50% pyrethins)	2.70 „ „ „
*Iso*propyl alcohol	67.05 „ „ „
	100.00 parts by weight

EXAMPLE II

"KELREZ" S.S.11	55.0 parts by weight
Neopynamin	0.7 „ „ „
Piperonyl butoxide	7.0 „ „ „
*Iso*propyl alcohol	37.3 „ „ „
	100.0 parts by weight

EXAMPLE III

"KELREZ" SS. 34	55.0 parts by weight
Pybuthrin (*see note below)	8.2 „ „ „
*Iso*propyl alcohol	36.8 „ „ „
	100.0 parts by weight

* The pybuthrin used consisted of 1.4 parts by weight of pyrethrum extract (50% pyrethrins) and 6.8 parts by weight of piperonyl butoxide.

EXAMPLE IV

"KELREZ" SS. 11	55.0 parts by weight
Malathion	10.2 „ „ „
*Iso*propyl alcohol	34.8 „ „ „
	100.0 parts by weight

EXAMPLE V

Styrene/nonanol acid maleate copolymer	30.25 parts by weight
Allethrin	1.40 „ „ „
*Iso*propyl alcohol	68.35 „ „ „
	100.00 parts by weight

EXAMPLE VI

"KELREZ" SS. 34	55.0 parts by weight
Sevin	6.8 „ „ „
Co-solvent, e.g. dimethyl sulphoxide	10.0 „ „ „
*Iso*propyl alcohol	28.2 „ „ „
	100.0 parts by weight

EXAMPLE VII

Copolymer of styrene/methylmethacrylate with ethyl acid fumarate	30.25 parts by weight
Bromophos	10.20 „ „ „
*Iso*propyl alcohol	59.55 „ „ „
	100.00 parts by weight

EXAMPLE VIII

"KELREZ" SS.34	55.0 parts by weight
Sumithion	3.4 „ „ „
*Iso*propyl alcohol	41.6 „ „ „
	100.00 parts by weight

In order to investigate the insecticidal efficacy of the compositions of this invention various trials have been carried out under conditions simulating, though more severe than, those likely to be encountered in normal everyday situations. Details of one such trial, regarded as typical of the results secured, are set out below:—

EXAMPLE IX — *Investigation of Insecticidal Efficacy*

Twelve cardboard cartons were coated with the composition of Example III, to give a deposit of 50 mg. of pyrethrins and approximately 500 mg. of piperonyl butoxide per sq. metre. These cartons were then filled with bags of wholemeal flour and placed for 6 months, in an infested store, in the form of a wooden building 8′ x 8′ x 10′, lined with shelves and on a concrete base, maintained continuously at a temperature of 75°F and at 65% Relative Humidity, heavily infested at commencement and thereafter regularly re-infested at weekly intervals with the insects specified below. Twelve uncoated cartons were likewise filled and placed in the same infested store.

At the end of this period all the cartons were examined and the results are shown in the table below:—

UNCOATED CARTONS

Carton	Between carton and paper liner	In Wholemeal flour
1	22 living moth larvae 3 moth pupae 3 live moths 3 dead moths	95 living moth larvae 1 adult *Tribolium* spp. 4 moth pupae Very heavy moth webbing
2	3 living moths 160 dead moths 3 pupae 1 living moth larvae	Very heavy webbing and large numbers of live and dead moths, and live larvae and pupae
3	4 living moths 8 dead moths	Some webbing 6 dead moths 66 living moth larvae
4	35 living moths 10 dead moths 8 living moth larvae 3 moth pupae	Very heavy webbing and large numbers of live and dead moths, live larvae and pupae
5	20 living moths 10 dead moths 7 living larvae	80 living moth larvae 15 adult *Tribolium* spp. 18 moth pupae Heavy webbing
6	36 living moths 27 dead moths 15 live larvae 3 moth pupae	Very heavy webbing and extreme infestation of moths and *Tribolium* spp.
7 8 9	Very large number of moth larvae, adults and pupae	Very heavy webbing and infestation of moths
10	8 live moths 2 dead moths 3 live moth larvae	36 live moth larvae 7 moth pupae 32 living adult *Tribolium* spp.
11	2 live moths	Light webbing 8 living moth larvae 2 moth pupae 29 adult *Tribolium* spp. Numberous live larvae of *Tribolium* spp.
12	Large number of moth larvae, adults and pupae	Extreme infestation of moth larvae together with heavy webbing

COATED CARTONS

1	1 dead adult moth	1 dead adult *Tribolium* spp.
2	1 living adult *Tribolium* spp.	Insect-free
3		
4		
5	Insect-free	Insect-free
6		
7	1 live adult moth 2 live adult *Tribolium* spp.	2 moth pupae 3 live adult *Tribolium* spp.
8		
9		
10	Insect-free	Insect-free
11		
12		

These results indicate that all twelve uncoated cartons were infested with the moths *Plodia interpunctella* and *Angasta kuhniella* and the flour beetle *Tribolium casteneum* All twelve coated cartons were relatively free from infestation. Throughout the trial the coatings maintained their high gloss.

It will be noted that the compositions described in Examples I to VIII above are all ready for application to paper or like packaging material without further adjustment in viscosity, but it will of course be understood that the invention also embraces concentrates such as may be sold in commerce which before use in conventional paper varnishing machinery will require dilution, for instance with isopropyl alcohol, to bring their viscosities to the desired value.

WHAT WE CLAIM IS:—

1. Insecticidal coating compositions, especially adapted for use upon fibrous packaging material such as paper, cardboard and the like, comprising one or more insecticides dissolved and/or dispersed in a film-forming synthetic resin consisting wholly or predominantly of a copolymer of styrene with a dibasic unsaturated aliphatic acid half-ester.

2. Insecticidal compositions as claimed in claim 1, wherein the insecticide(s) is/are one or more of the following, namely pyrethrum, neopynamin, allethrin and other pyrethrinoid insecticides as herein defined, either with or without a synergist, as well as malathion, vapona, sevin, bromophos and sumithion.

3. Insecticidal compositions as claimed in either of the preceding claims, wherein there is also a co-solvent for the insecticide(s).

4. Insecticidal compositions as claimed in any of the preceding claims, wherein the insecticide(s) employed has/have an LD_{50} (rat: oral) of at least 400 mg/kg.

5. Insecticidal compositions as claimed in any of the preceding claims wherein the insecticide(s) employed has/have an LD_{50} (rat: oral) of 500 mg/kg or more.

6. Insecticidal coating compositions, especially adapted for use upon fibrous packaging material such as paper, cardboard and the like, comprising one or more pyrethrinoid insecticides (as defined herein) dissolved and/or dispersed in a film-forming synthetic resin consisting wholly or predominantly of a copolymer of styrene with a dibasic unsaturated aliphatic acid half-ester.

7. Insecticidal compositions as claimed in claim 6, wherein there is also included a synergist based on the methylene dioxy phenyl structure.

8. Insecticidal compositions as claimed in claim 7, wherein the synergist is piperonyl butoxide.

9. Insecticidal compositions as claimed in any of the preceding claims, wherein there is also included *iso*propyl alcohol as a component solvent.

10. Insecticidal compositions as claimed in any of the preceding claims, wherein the proportions of the two co-polymerizing components are in the weight ratio range of from 20:80 to 80:20.

11. Insecticidal compositions as claimed in claim 10, wherein the weight ratio is substantially 50:50.

12. Insecticidal compositions as claimed in any of the preceding claims, wherein the dibasic unsaturated aliphatic acid employed to form the co-polymer half-ester component is maleic acid.

13. Insecticidal compositions as claimed in any of the preceding claims, wherein the alcohol employed to form the co-polymer half-ester component is an unsubstituted straight chain alcohol having from 1 to 18 carbon atoms.

14. Insecticidal compositions as claimed in claim 13 wherein the alcohol is ethanol or *n*-butanol.

15. Insecticidal compositions as claimed in any of the preceding claims, wherein the resin component also includes a cross-linking catalyst.

16. Insecticidal compositions as claimed in claim 15, wherein the catalyst is benzoyl peroxide.

17. Insecticidal compositions as claimed in any of the preceding claims, ready for application to fibrous packaging material such as paper by conventional paper varnishing machinery, which have a viscosity sufficient to allow a full discharge time of between 25 and 100 seconds from a No. 4 Ford Cup.

18. Insecticidal compositions as claimed in any of the preceding claims and substantially as described herein, especially with reference to the Examples.

19. A process for the preparation of an insecticidal composition as defined in any of the preceding claims, substantially as described herein.

20. Insecticidal compositions, whenever prepared by a process as claimed in claim 19.

21. A method of manufacturing paper or like fibrous packaging material which includes the step of applying to said packaging material by conventional paper varnishing machinery a coating of an insecticidal composition as claimed in claim 17 and which has a viscosity of from 40 to 220 centipoises, and thereafter drying said composition to form a glossy insecticidal coating upon the packaging material.

22. A method as claimed in claim 21, for the manufacture of foodstuff packaging material, in which the insecticide(s) incorporated in said coating composition is/are one or more pyrethrinoid insecticides (as defined herein) having a low mammalian toxicity, either with or without a synergist based on the methylene dioxy phenyl structure.

23. Packaging material whenever manufactured by a process as claimed in claim 21 or claim 22.

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